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Work on this program has been performed by personnel at the Hughes Research Laboratories as well as Dr. Alexander Borshchevsky, Center for Materials Research, Stanford University, and Professor Paul L. Richards, Department of Physics, University of California at Berkeley.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The objectives of this program are to find and develop new IR transmitting materials and to provide new data on the electrooptic (EO) properties of those most likely to have an EO coefficient an order of magnitude higher than materials currently in development for tunable filters. The main technical problems anticipated include the synthesis and single-crystal growth of these materials: many are poorly characterized and others have high melting points or melt incongruently. Our

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approach will overcome these obstacles by first synthesizing approximately 20 polycrystalline samples. Subsequently, their dielectric constants at low and ambient temperatures will be determined, and the two best materials of the survey will be grown as single crystals (second year of the program).

During the last quarter, several new multinary compounds were synthesized and evaluated. These compounds included $CdIn_2Te_4$, Cu_2GeS_3, Cu_2GeTe_3, and $Cu_2CdGeTe_4$. Among those characterized for dielectric constant and loss tangent, $CdIn_2Te_4$ was measured to have a low-frequency (10-kHz) dielectric constant of 456.9, an order of magnitude larger than those determined for other compounds on this program. This makes $CdIn_2Te_4$ a clear first choice for single-crystal growth and further EO and electrical property evaluation. A repeated measurement of $ZnGa_2S_4$ confirmed previously measured values at 10 kHz; the value of the dielectric constant is essentially equivalent to that of a newly synthesized compound, Cu_2GeS_3. Differential thermal analysis of physical properties as well as thermochemical properties of both of these ternary compounds will be pursued to select the one that appears easier to synthesize in single-crystal form. The quarternary compound $Cu_2CdGeTe_4$, which was measured to have a somewhat higher dielectric constant than the two ternary compounds $ZnGa_2S_4$ and Cu_2GeS_3, requires further investigation because of the persistent presence of uncombined CdTe.

Work during the next quarter will emphasize the growth and characterization of single-crystal $CdIn_2Te_4$.

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SECTION 1

INTRODUCTION AND SUMMARY

A. PROGRAM OBJECTIVES

The objectives of this program are to find and develop new IR transmitting materials and to provide new data on the electrooptic (EO) properties of those most likely to have EO coefficients an order of magnitude higher than materials currently in development for tunable filters. The main technical problems anticipated include the synthesis and single-crystal growth of these materials: many are poorly characterized and others have high melting points or melt incongruently. Our approach will overcome these obstacles. First, we will synthesize 20 polycrystalline samples. Then the dielectric constant of each, at both low and ambient temperatures, will be determined, and the two best materials of the survey will be grown as single crystals (second year of the program).

B. SUMMARY

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SECTION 2

MATERIALS PREPARATION AND CRYSTAL GROWTH

A. $CdIn_2Te_4$

A small, cone-shaped ingot ∿1.3 cm in length and ∿1.3 cm in maximum diameter was grown from solution using In_2Te_3 essentially as the solvent. Both X-ray diffraction analysis (see pattern, Figure 1) and microscopic observation indicated that the ingot is single phase and appears to be a single crystal. The chemical composition was determined to be 13 at.% Cd, 29 at.% In, and 58 at.% Te, indicating an off-stoichiometric composition of $CdIn_{2.23}Te_{4.46}$ lying on the In_2Te_3-rich side of the existence region in the pseudo-binary phase equilibrium diagram CdTe-In_2Te_3. The crystal is tetragonal.

B. Cu_2GeS_3

A polycrystalline ingot of Cu_2GeS_3 was obtained by quenching a melt of that composition. X-ray diffraction indicated the presence of at least one additional phase. Table 1, a compilation of lattice parameters of $A_2^{I}B^{IV}C_3^{VI}$ compounds with literature references (compiled by A. Borshchevsky, Stanford University) indicates the existence of solid phase transitions and a variety of opinions on crystal class of the low-temperature form. The ingot and the powder were annealed. After annealing, no changes were observed in the ingot that contains a second phase, but minor changes were observed in the powder. Published phase diagrams indicate that this compound is a peritectic that is possible to grow using a GeS_2-rich melt. An X-ray diffraction pattern for Cu_2GeS_3 (Figure 2) shows the X-ray diffraction pattern of the high-temperature distorted-cubic phase quenched from the melt (Figure 2(a)); the annealed powder pattern (450°C for 500 hr) is shown in Figure 2(b). The phase transition is reported to be at 670°C. Although there is a slight difference in the patterns, we have not observed any definite evidence of a low-temperature phase.

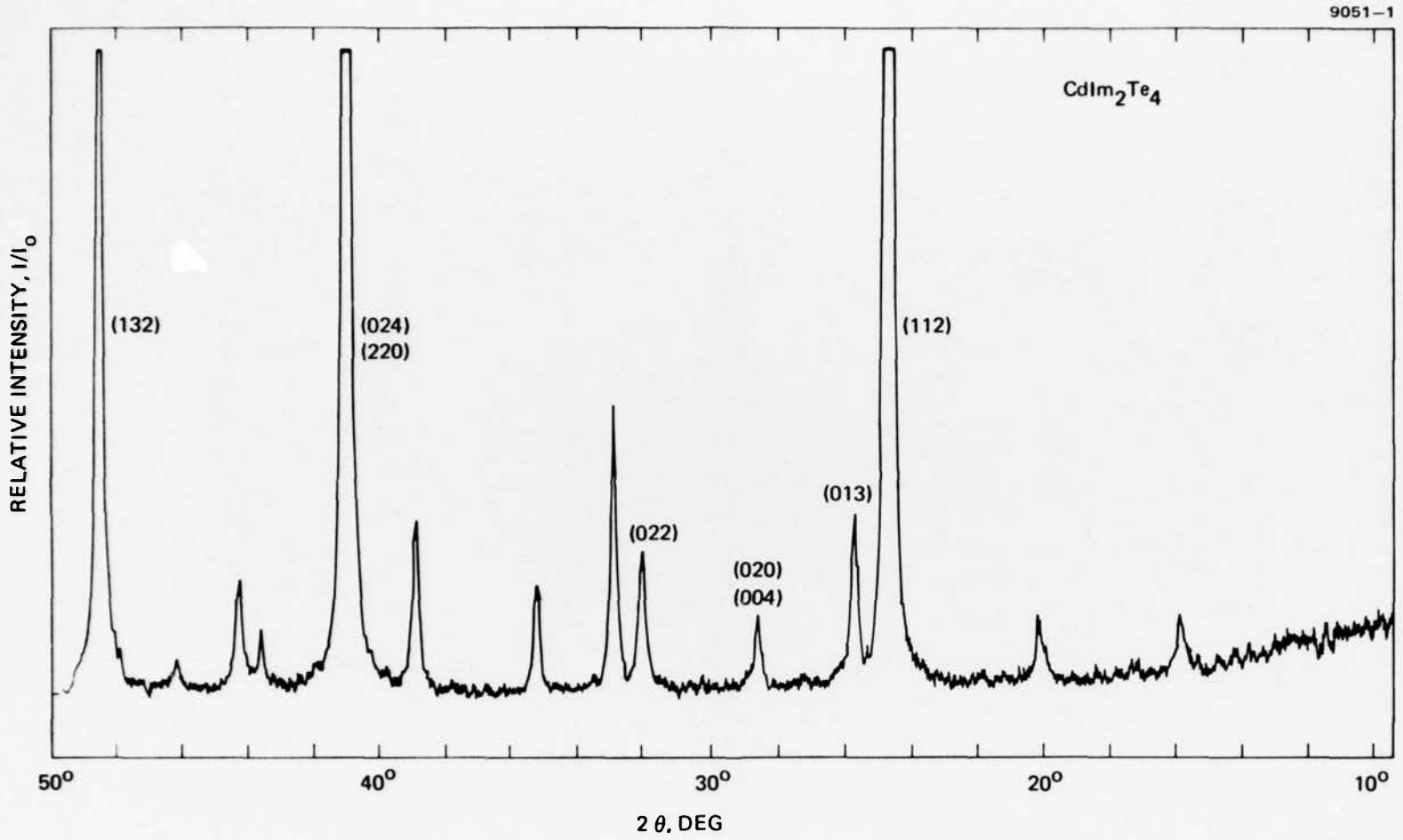
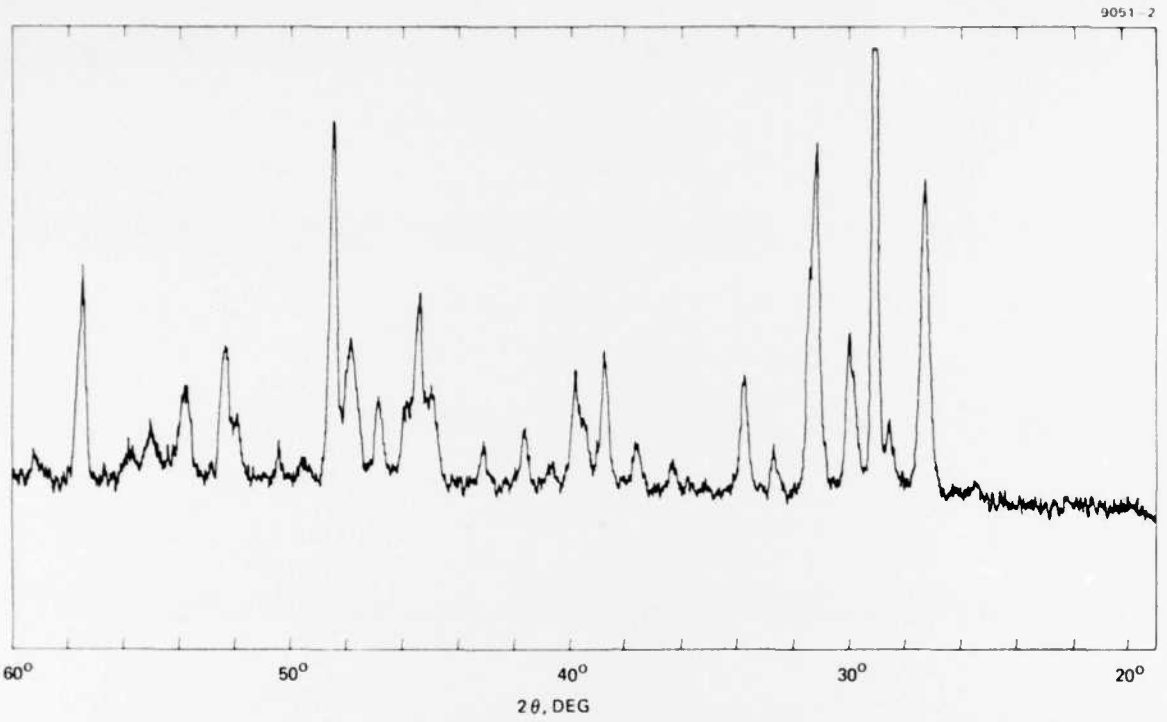


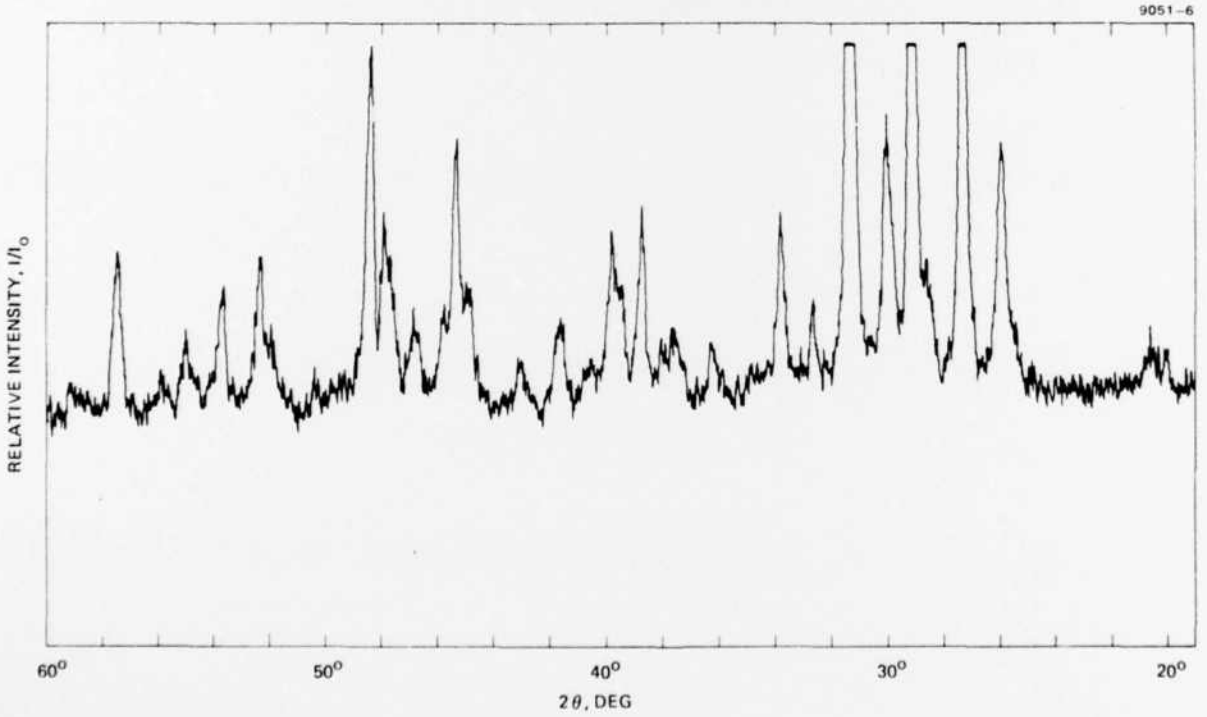
Figure 1. X-ray diffraction pattern of $CdIn_2Te_4$.

Table 1. Lattice Parameters of $I_2IV\ VI_3$ Compounds

Compound	Crystal System	a, Å	b, Å	c, Å	β, deg	Reference
Cu_2SiS_3 (H.T.)	Hex	3.684		6.044		1
Cu_2SiS_3 (L.T.)	Tetr	5.290		5.078		1
	Ortho	11.21	12.04	6.03		2
	Mono	11.51	5.34	8.16	98.95	2
	Ortho	10.981	6.416	6.046		3
Cu_2SiSe_3	Mono	12.10	5.62	8.61	99	2
Cu_2SiTe_3	Mono	12.86	6.07	9.05	99	2
	Cubic	5.93				1
Cu_2GeS_3 (H.T.)	Cubic	5.317				1
Cu_2GeS_3 (L.T.)	Tetr	5.326	5.219			1
	Tetr	5.320	10.41			2
	Ortho	11.321	3.766	5.21		3
	Cubic	5.30				4
	Mono	6.433	11.300	7.533	125.17	5
	Mono	7.464	22.38	10.64	91.17	6
Cu_2GeSe_3	Tetr	5.595	5.482			1
	Tetr	5.590	10.97			2
	Ortho	5.591	5.562	5.488		7
	Cubic	5.55				4
	Tetr	5.591	5.485			8
	Ortho	11.860	3.960	5.485		3
Cu_2GeTe_3	Tetr	5.956	5.926			1
	Tetr	5.916	11.85			2
	Cubic	5.95				4
Cu_2SnS_3	Cubic	5.445				1
	Tetr	5.426	10.88			2
	Cubic	5.43				4
Cu_2SnSe_3	Cubic	5.696				1
	Tetr	5.689	11.37			2
	Cubic	5.68				4
	Cubic	5.6877				8
Cu_2SnTe_3	Cubic	6.047				1
	Tetr	6.048	12.11			2
	Cubic	6.04				4



(a) As-grown sample



(b) After annealing

Figure 2. X-ray diffraction pattern of Cu_2GeS_3.

C. Cu_2GeTe_3

The structure as indicated by X-ray diffraction analysis appears to be cubic with a = 5.95 ± 0.02 Å. No evidence of the reported tetragonal phase is indicated in the X-ray diffraction patterns (Figure 3) for as-grown and annealed (450°C for 500 hr) samples. However, differential thermal analysis (DTA) indicates the existence of a solid phase transformation (exact temperature to be determined) and a congruently melting compound at 490°C. The material contains a small amount of a second phase both before and after annealing. The material we see appears to be the high-temperature cubic phase. Although the literature (see Table 1) is not precise on that matter, there are reports of the observation of a tetragonal phase. Additional DTA work is required if the compound appears interesting (i.e., has a high dielectric constant).

D. $Cu_2CdGeTe_4$

As-grown and annealed samples of the reported quaternary compound both show by X-ray diffraction analysis (Figure 4) free CdTe. The annealed sample (450°C for 500 hr) shows (Figure 4(b)) reduced CdTe peaks and a shift (change in lattice parameters) from the as-grown sample (Figure 4(a)), which may indicate that continued annealing will yield the quaternary from a composition that looks (as-synthesized, Figure 4(a)) like the ternary Cu_2GeTe_3 plus CdTe. The presence of additional phases in the material also was observed both before and after annealing; perhaps this indicates two additional phases plus CdTe. DTA data showed at least three phase transformations: 786, 523, and 513°C.

E. $ZnGa_2S_4$

Initial DTA investigation of $ZnGa_2S_4$ indicated a melting point in excess of 1200°C (limit of current DTA apparatus) and a possible phase transition above 1000°C. Attempts at single-crystal growth by vapor transport have shown extremely slow transport and tendencies toward polycrystalline growth. We will investigate, by DTA, suitable solution growth conditions for $ZnGa_2S_4$ using zinc as solvent.

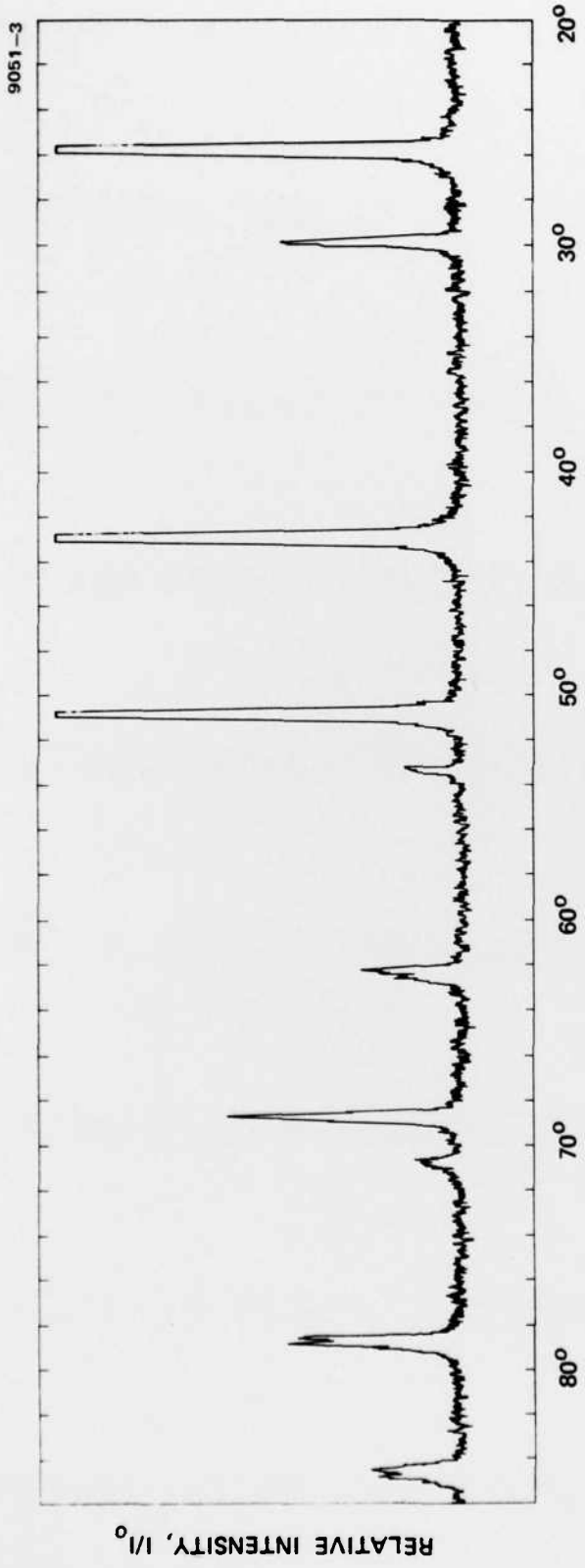
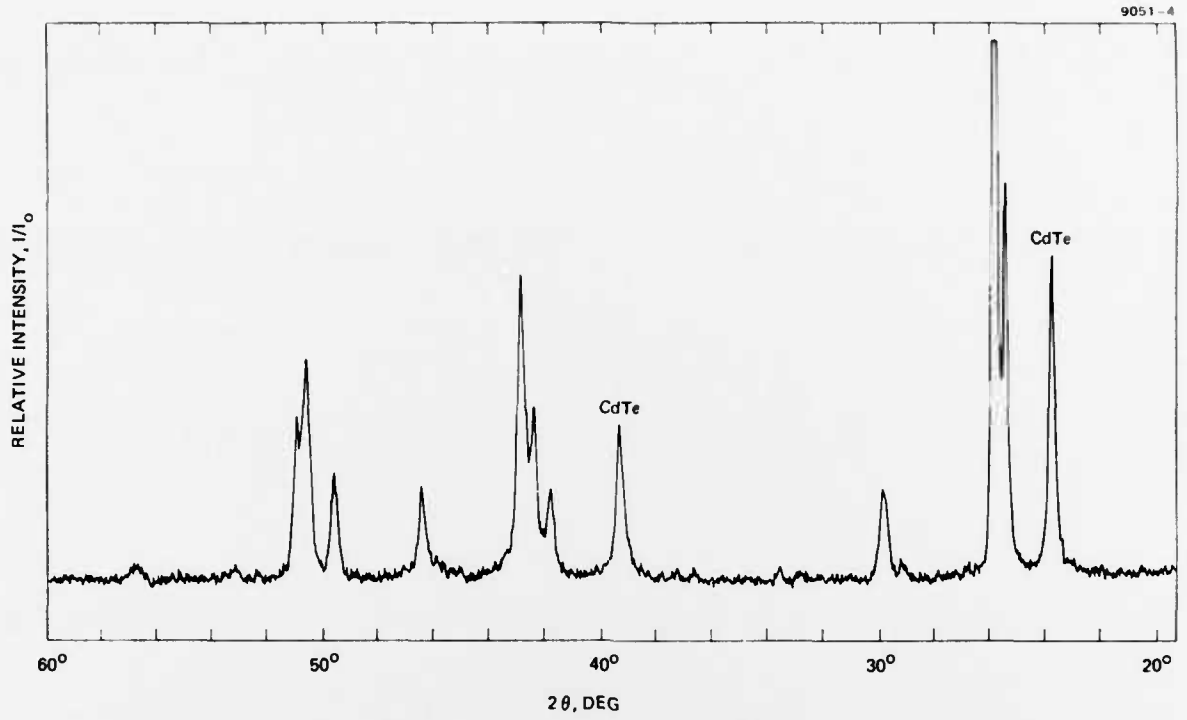
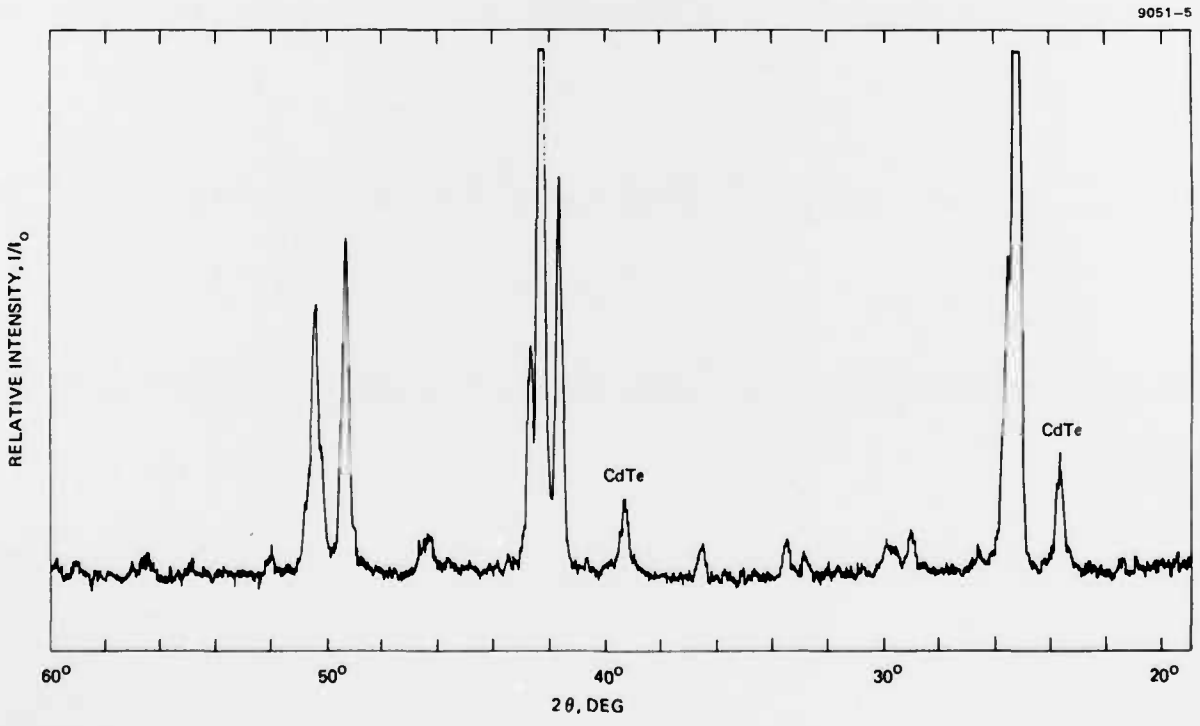


Figure 3. X-ray diffraction pattern of cubic Cu_2GeTe_3.



(a) As-grown sample



(b) After annealing

Figure 4. X-ray diffraction pattern of $Cu_2CdGeTe_4$.

SECTION 3

MATERIALS EVALUATION

A. DIELECTRIC CONSTANT MEASUREMENTS

Dielectric constants and loss tangents (tan δ) were determined for several of the recently synthesized compounds. The data are shown in Table 2.

Table 2. Dielectric Constant and Loss Tangent at 10 kHz

Material	E_s	tan δ
Cu_2GeS_3	49	0.00028
$Cu_2CdGeTe_4$	60.3	0.00364
$CdIn_2Te_4$	456.9	0.00515
$ZnGa_2S_4$	46.3	0.499

The recent data indicate an order-of-magnitude increase in dielectric constant (the largest that we have yet observed) over previously selected samples (e.g., $ZnGa_2S_4$). This large dielectric constant was measured in a sample of tetragonal $CdIn_2Te_4$ as described earlier in this report. We plan to pursue single-crystal growth and subsequent evaluation of the EO and possible ferroelectric properties of this material. The ternary compound $ZnGa_2S_4$ (previously measured and reported in Quarterly Report No. 5) and Cu_2GeS_3 have essentially equivalent dielectric constants. The repeated measurement on $ZnGa_2S_4$ was in good agreement with measurements reported earlier. We have started DTA measurements on $ZnGa_2S_4$ to determine its melting point as well as to evaluate the possibility of growth from zinc solution. We plan to use DTA to make similar determinations for Cu_2GeS_3. The latter crystal, Cu_2GeS_3, as reported above has shown solid transitions. Initially, the compound which appears to be more amenable to single-crystal growth will be pursued.

The quarternary compound $Cu_2CdGeTe_4$ is derived from the tetragonal chalcopyrite Cu (Ga or In) Te_2 by substitution of a Group II and a Group IV atom (Cd and Ge, respectively) for two Group III atoms (Ga or In) in the lattice. However, there is evidence (see Figure 4) of the presence of free CdTe, which persists even after long-term annealing, although at a significantly diminished level. This material requires additional investigation before any valid conclusions can be drawn.

REFERENCES

1. J. Rivet, J. Flahaut, and P. Laruelle, Compt. Rendue Acad. Sci. (Paris) 257, 161 (1963); J. Rivet, Amm. Chim. (Paris) 10, 5 and 6, 243 (1965).

2. H. Hahn, W. Klinger, P. Ness, and H. Schulze, Naturwissen 53, 18 (1966).

3. E. Parthé and J. Garin, Monatshelfte für Chemie 102, 1197 (1971).

4. L.S. Palatnik, V.M. Koshkin, L.P. Galchinetski, V.I. Kolesnikov, and Yu. V. Komnik, Sov. Phys. Solid State 4, 1052 (1962).

5. G.K. Averkieva, A.A. Viapolin, and N.A. Gorunova, "Soviet Research on New Materials," Ed. D.N. Nasledov and N.A. Goryunova, Consultants Bureau, New York (1965).

6. M. Khanafer, O. Gorochov, and J. Rivet, Mat. Res. Bull. 9, 1543 (1974).

7. B.R. Pamplin, Scientific Advisers Report SAMSS 5/65 (1965).

8. B.B. Sharma, PhD. Thesis, University of Delhi (1979).